Deposition of Silicon Dioxide Films Using Electron Beam-Generated Plasmas

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Key Words: Plasma source, Electron beam, PECVD, Hollow cathode

ABSTRACT

The Naval Research Laboratory is developing a plasma processing system to deposit SiO_2 films and coatings. These plasmas are produced by high-energy (≈2 keV) electron beams and have numerous properties that separate them from conventional plasma sources and make them well suited for plasma enhanced chemical vapor deposition (PECVD) applications. These attributes as well as the initial results of SiO_2 film production using mixtures of argon, oxygen, and tetraethoxysilane (TEOS) are discussed in terms of system operation, plasma characterization, and film properties.

INTRODUCTION

The Naval Research Laboratory has developed a materials processing system based on electron beam-generated plasmas for use in range of processing applications [1]. When high-energy (≈ 2 keV) electron beams are used as the primary ionization source, the resultant plasmas have unique characteristics when compared to conventional low-pressure plasma sources.

Low electron temperature. Conventional plasma discharges rely on externally applied electric fields to raise the plasma electron temperature so that a fraction of those electrons are energetic enough to ionize the gas and sustain the plasma. Because the high-energy electron beam ionizes the gas, electron beam-generated plasmas require no heating of the plasma electrons, which are quickly cooled by elastic and inelastic collisions. The resulting plasma electron temperatures are found to be 1.0 eV or lower [2], depending on background gas. The temperature in molecular gas backgrounds tends to be lower than in noble gases due to the availability of low-energy excitation states. Since the electron temperature determines the plasma potential [3], ions incident to grounded surfaces will also exhibit low energies [4], typically below 5 eV.

Efficient and controllable ion production. For multi-kilovolt electrons passing through a gas, ionization is the dominant mechanism with the cross-sections being similar for most gases. Thus, little energy is consumed by non-ionizing collisions and species generation can be regulated by adjusting the background gas concentrations. This is in contrast to conventional discharges where the dominant inelastic collisions consume most of the delivered energy and ion production favors the species with the lowest ionization potential.

Localized and scalable plasma source. The beam thickness and width are determined by the electron beam source and the length is determined by the beam energy and operating pressure. The plasma production region is limited to the beam volume, which is well defined and uniform when the beam is magnetically collimated. Hence, the dimensions of the plasma source are tied to the electron beam dimensions which makes scaling straightforward. Outside the beam channel, the plasma density and ion composition are altered by ion-electron, ion-neutral, and ion-ion reactions. Thus, electrodes (or substrates) can be independently positioned to take advantage of the changes in the outwardly diffusing flux of ions and radicals. In conventional discharges, the boundaries of the ionization region are not well defined and increasing the dimensions in a uniform manner can be problematic.

While these attributes can be advantageous in a number of processing applications, they are particularly well suited for plasma enhanced chemical vapor deposition (PECVD) applications using large area substrates and processes that are not compatible with large ion energies. It is with these ideas in mind that a PECVD process is being developed for the deposition of SiO_x films and coatings using tetraethoxysiloxane (TEOS) as the silicon source. The initial plasma diagnostics and results for films deposited on silicon substrates are discussed.

EXPERIMENT

Plasma Diagnostics

The experimental apparatus has been discussed previously [5] and is shown in the schematic of Figure 1. To date, investigations have been limited to plasmas produced in mixtures of argon and oxygen without the TEOS precursor. High purity argon and oxygen were introduced by mass flow controllers at 50 sccm's each and the operating pressure of 50 mTorr was achieved by throttling the turbo pump. A beam of energetic electrons was produced by a linear hollow cathode [6] pulsed to 2 kilovolts for 2 ms at a 20% duty factor. The emergent beam passed through a slot in a grounded anode and was then terminated at a second grounded anode located further down-

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stream. The electron beam volume between the two anodes defines the ionization source volume, with the dimensions set by the slot size (1 cm x 25 cm) and the anode-to-anode length (43 cm). Beam spreading from collisions with the neutral background was largely eliminated by a coaxial magnetic field of 150 Gauss that was produced by a set of external magnetic field coils.

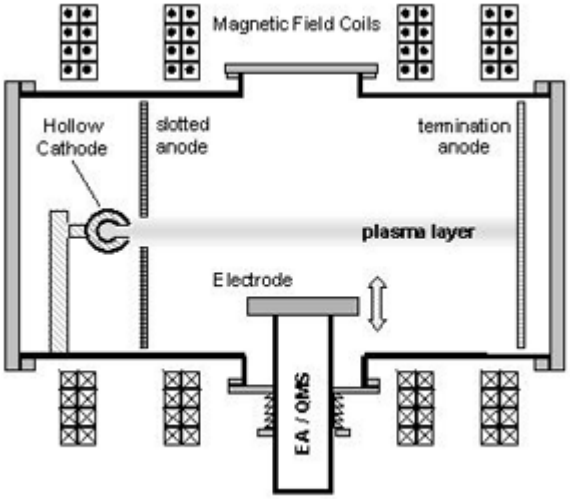

Figure 1. The diagnostic chamber.

Ion energy distributions and fluxes were measured at the center of a grounded 5.7 cm diameter stainless steel electrode using a Hiden EQP 300 Plasma Probe. Ions enter the EQP through a 20 mm diameter aperture located in the center of the electrode and are first energy selected by an electrostatic energy analyzer (EA) and then mass filtered by a quadrupole mass spectrometer (QMS). The energy analyzer has a fixed resolution ($D E/E_t$) that provides an uncertainty in energy of approximately ± 0.15 eV. Because the system is pulsed, all data acquisition is time resolved and the gating techniques have been described elsewhere [7]. The EQP has not been calibrated to determine the absolute flux of each species, so the intensity of the measured signal is reported in arbitrary units.

Film Production

A cylindrical reactor consisting of a similarly sized electron beam source as the experimental configuration of Figure 1 was used for the deposition work. The EQP stage was replaced by a biasable, temperature controlled stage upon which pieces of p-type <100> silicon wafers (resistivity 1-20 Ω-cm) were mounted. The substrates were dipped in a 5% HF solution immediately before mounting to the stage and placing in vacuo. The stage was located 2.5 cm from the electron beam axis.

At room temperature, TEOS is a liquid with an appreciable vapor pressure (~ few torr). It was introduced to the system by flowing a fixed amount of argon through a bubbler kept at 18 Torr by a throttle valve between the bubbler and processing chamber. The argon flow through the TEOS bubbler and a separate argon line directly to the chamber were set to total 50 sccm, which allowed a wide range of TEOS gas flow conditions. The TEOS sample was degassed and the gas lines were purged two times before each run. The TEOS gas line to the chamber was heated to prevent condensation. The other reactive process gas was oxygen, also set at a fixed flow of 50 sccm, bringing the total gas flow to 100 sccm for the process.

Inside the chamber, the TEOS was introduced approximately 1 cm in front of the sample stage. The oxygen and independent argon gas lines were introduced approximately 40 cm away at the wall of the chamber, with no special relation to the substrate or e-beam. The sample stage was electrically grounded for this work and could be heated or cooled. The stage temperature was reached rapidly (20-30 min) and allowed to equilibrate for 10 min. As an additional cleaning step before any TEOS was introduced, a 50 mTorr argon/oxygen plasma (50 sccm each) was run for 20 minutes. TEOS was then introduced by opening the bubbler isolation valve and adjusting the two argon flows to maintain a 100 sccm total. The growth continued at 50 mtorr for 3 to 3.5 hours and was monitored with an in situ HeNe laser reflectometer. After deposition, the TEOS reservoir was again isolated from the system and an argon/oxygen post-treatment plasma was again run for 20 minutes. For all plasma steps, the e-beam was modulated in time, having a fixed 2 ms duration and 20% duty factor.

After the plasma post-treatment, the stage heating or cooling was turned off and the sample was allowed to come to room temperature. The sample was removed from vacuum and the film thickness was measured using a white-light spectrophotometer. The composition of the SiO_x films were analyzed by FTIR (Nicolet Magna 750; MCT detector and 4 cm^{-1} resolution) and by wet etching in a "P-etch" solution [8] of 15 HF:10 HNO_3: 300 H_2O (by volume).

RESULTS AND DISCUSSION

Plasma Diagnostics

Ion energy distributions measured at a grounded electrode located 2.5 cm from the electron beam axis are shown in Figure 2. O_2^+, Ar^+, and O^+ are the dominant ion species in these plasmas, as indicated in the figure inset. Both the energy distributions and mass spectrum were accumulated during a gate that spanned most of the 10 ms period. The energy distributions are characterized by low maximum and most probable energies; indicative of low plasma potentials and thus low electron temperatures. Although no Langmuir probe measurements were performed in these plasmas, it can be assumed that the electron temperature will be similar to that measured in nitrogen plasmas, which were found to be approximately 0.5 eV [9], a value compatible with the measured ion energy distributions.

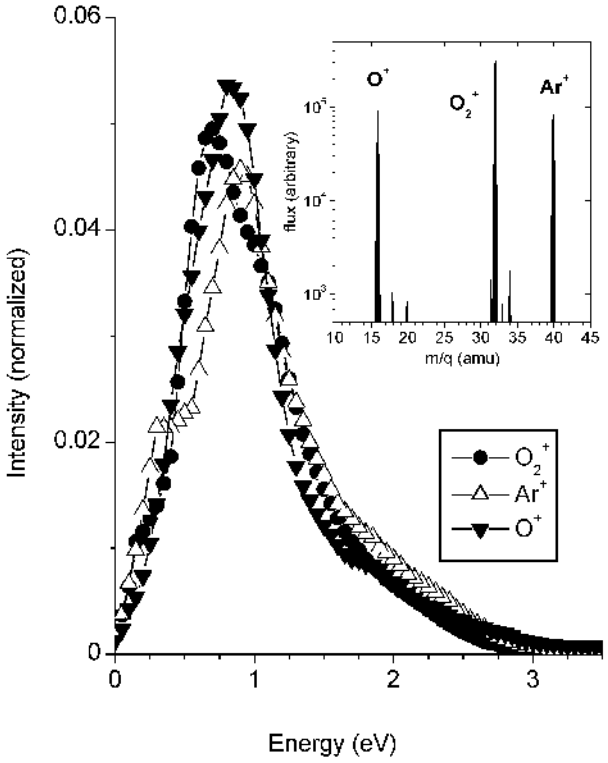

Figure 2. Ion energy distributions sampled from plasmas produce in mixtures of argon and oxygen and measured at an electrode located 2.5 cm from the electron beam axis. Inset: Mass spectrum acquired under the same conditions.

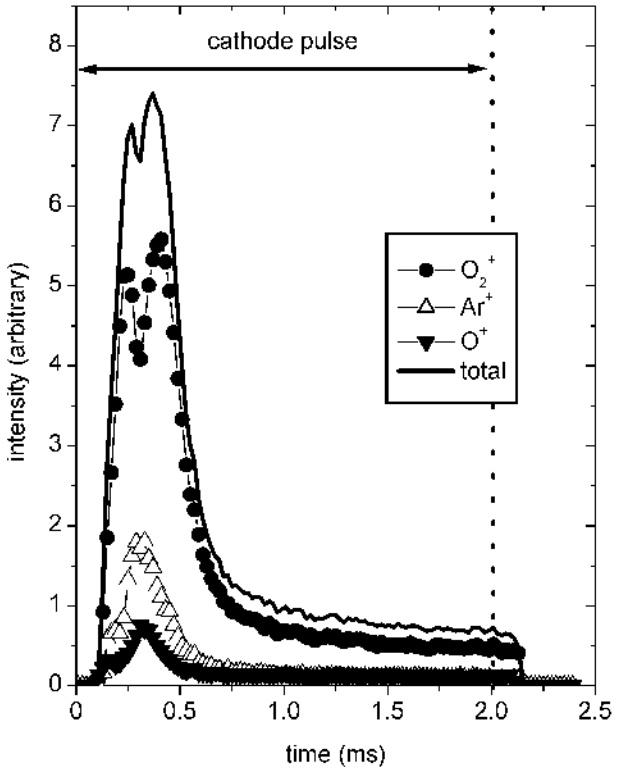

Figure 3. Time-resolved ion fluxes sampled from plasmas produced in mixtures of argon and oxygen and measured at an electrode located 2.5 cm from the electron beam axis.

Shown in Figure 3 are the relative ion fluxes as function of time as well as their sum. The slight delay in time is due to the ion time of flight in the EQP. The peak in ion intensity during the first third of the pulse width is not fully understood, but could be due to a combination of effects, consisting namely of cathode operation and gas phase reactions. Given the large concentration of oxygen and its known influence on secondary electron emission even at low ion impact energies [10], it is not unreasonable for the electron beam produced by pulsing the hollow cathode to exhibit strong temporal dependencies. Additionally, electron-ion recombination ($e + O_2^+ \rightarrow 2O$; $k_r \sim 10^{-8}$ cm^3/s) [11] and charge exchange reactions ($Ar^+ + O_2 \rightarrow Ar + O_2^+$, $O^+ + O_2 \rightarrow O + O_2^+$; $k_r \sim 10^{-11}$ cm^3/s) [12] will lead to a temporal and spatial variation in all species.

The influence of these gas phase reactions is seen in Figure 4, where the relative and total ion fluxes as a function of electrode position are shown. As previously noted, ionization by a 2 keV electron beam will produce ion densities in proportion to the background gas density. Despite equal quantities of argon and oxygen, O_2^+ ions are, by far, the dominant species at all electrode locations and is due to the destruction of Ar^+ ions by charge exchange with the oxygen background. The rapid reduction in the total ion flux with increasing distance, on the other hand, is caused by the destruction of O_2^+ ions via electron-ion recombination, which proceeds at a faster rate than the charge exchange reactions.

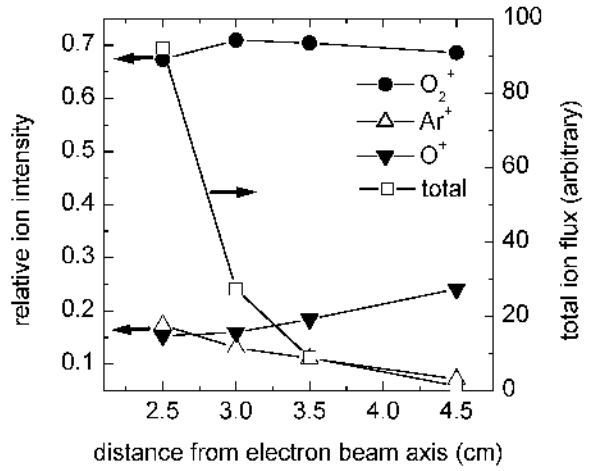

Figure 4. Ion fluxes sampled from plasmas produced in mixtures of argon and oxygen as function of electrode location.

In terms of deposition, these diagnostics indicate a very low-energy ion flux at grounded or floating substrate surfaces, making the plasma source useful when bombardment by high-energy ions is undesirable. If a more energetic ion flux is needed, the energy can be elevated by biasing the substrate. The spatial and temporal variations in the relative and total ion flux and add variables that might be used to optimize the process. Of course, the presence of TEOS will alter the relative ion fluxes and introduce a host of precursor related ions and radicals and so a direct comparison with the processing plasma here is limited. However, it is not expected to strongly impact the ion energies or the spatial profile of the total ion flux for the small TEOS quantities used in the deposition. A stronger influence on the temporal behaviors may be expected though.

Film Deposition

The focus of our work to date has been to optimize the growth rate and to assess the film quality. To that end, the deposition rate was studied as a function of TEOS flow and substrate temperature. All films were etched using the P-etch solution and the resulting etch rates varied between 100 and 200 nm/min, suggesting the films were porous. Ellipsometer measurements showed the index of refraction was found to be approximately 1.46 and the breakdown voltage was measured to be in excess of 6 MW/cm.

The growth rate as a function of TEOS flow is shown in Figure 5 for stage temperatures of 160°C and 300°C. The growth rate is determined using the total plasma exposure time (i.e. 20% of the total processing time). The TEOS flow is varied by adjusting the argon carrier flow with the oxygen and total flows held at a constant 50 and 100 sccm's, respectively. For the 300°C case, there was a clear leveling off of the deposition rate with TEOS flow, which didn't occur in the 160°C case. However, the lower temperature case possessed higher etch rates and less desirable film composition (see below). The Arrhenius plot of Figure 6 shows the growth rate as a function of stage temperature using a 2% TEOS flow. Shown in Figure 7 are FTIR measurements on a sampling of the films from Figure 6 along with a reference TEOS spectrum. The Si-O-Si band signatures are clearly present at 1100 cm^{-1} (stretch), 810 cm^{-1} (bend), and 450 cm^{-1} (rocking) for all process temperatures. What is also evident from the data is the evolution of Si-OH (3500 cm^{-1} and 930 cm^{-1}) and H-OH (3300 cm^{-1} and 1700 cm^{-1}) at lower stage temperatures. This suggests the films grown over the range of temperatures will vary in chemical structure and is important when considering the activation energy indicated in the Arrhenius plot (Figure 6). Finally, it should be noted that none of the films appear to contain any of the aliphatic chain groups ($-CH_2-CH_3$) of the precursor (2900 cm^{-1}).

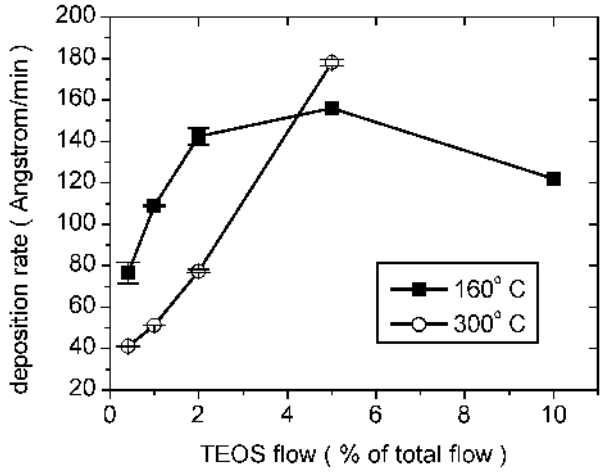

Figure 5. SiO_x deposition rate as function of TEOS flow.

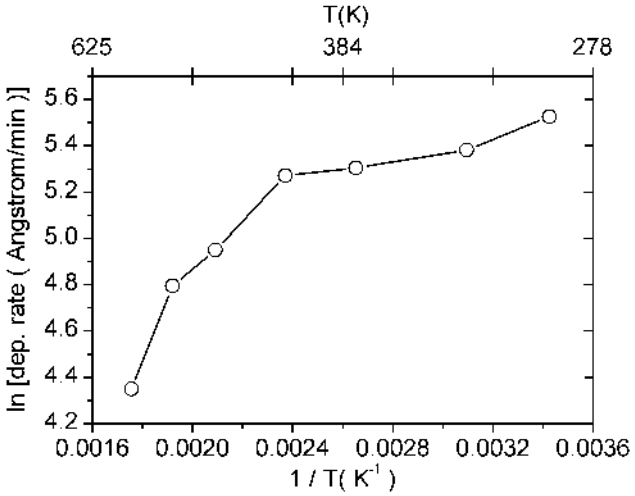

Figure 6. The temperature dependent SiO_x deposition rate using a 2% TEOS flow.

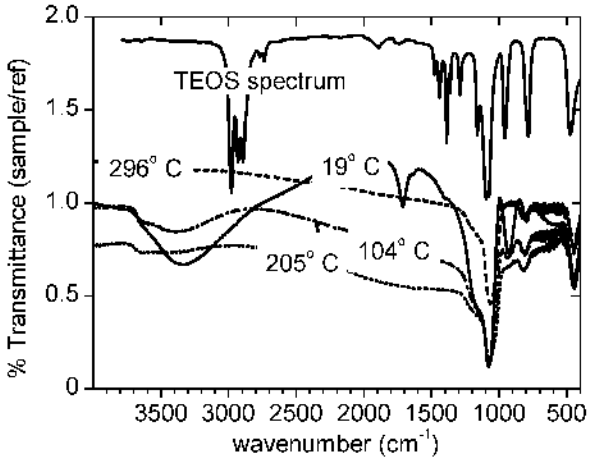

Figure 7. FTIR spectrum of films SiO_x deposited at various sample temperatures.

SUMMARY

Results from preliminary investigations of PECVD of SiO_x films and coatings using a pulsed, electron beam-produced plasma source were presented. *In situ* mass-resolved, ion energy distribution and flux measurements in plasmas produced in mixtures of argon and oxygen indicate the ion flux to adjacent, grounded electrodes was comprised of O_2^+, Ar^+, O^+ ions characterized by incident energies of a few eV. The total and relative ion fluxes have temporal variations and depend on the location of the electrode. For all times and locations the dominant species is O_2^+ ions. The initial deposition results show the deposition of SiO_x films proceed at rates that are dependent on both TEOS flow and stage temperature. The film chemistry was also found to depend on stage temperature. Future work includes additional diagnostics that will include the TEOS precursor and depositions with a biased stage to provide higher ion energies. The ultimate goal of this work is to develop a process compatible with the deposition of SiO_2 films on large area flexible substrates.

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